*Application of Cryogenic Grinding
to Achieve Homogenization
of Transuranic Wastes*

CONTENTS

FIGURES

FIGURES (continued)

FIGURES (continued)

FIGURES (continued)

TABLES

GLOSSARY OF TERMS

AO	always open
$CCl_2F-CClF_2$ (R113)	trichlorotrifluoroethane (R113)
CCl_4	carbon tetrachloride
cfm	cubic feet per minute
$CHCl_3$	chloroform
$CH_2:CHCl$	vinyl chloride
CH_2Cl_2	methylene chloride (dichloromethane)
CH_3Cl	methyl chloride (chloromethane)
CST	Chemical Science and Technology (Division)
CRC	*CRC Handbook of Chemistry and Physics*
DESO	double-end shutoff
DOE/RFFO	Department of Energy Rocky Flats Field Office
DP	differential pressure
ESA	Engineering Sciences and Applications (Division)
GN_2	gaseous nitrogen
HEPA	high-efficiency particulate air
ksi	1000 pounds per square inch
LANL	Los Alamos National Laboratory
LN_2	liquid nitrogen
NC	normally closed
NIST	National Institute of Standards and Technology
NMT	Nuclear Materials Technology (Division)
NO	normally open
PID	proportional integral derivative
ppm	parts per million

GLOSSARY OF TERMS (continued)

PRV	pressure relief valve
RFETS	Rocky Flats Environmental Technology Site
RGA	residual gas analizer
scfm	standard cubic feet per minute
TA-55	Technical Area-55, often used as shorthand for the Los Alamos Plutonium Facility
TCLP	total concentrate leachate procedure
VOC	volatile organic compound(s)
VOST	Volatile Organic Sampling Train
WC	water column

EXECUTIVE SUMMARY

Staff from the Nuclear Materials Technology (NMT) and the Engineering Sciences and Applications (ESA) divisions at Los Alamos National Laboratory (LANL) collaborated with staff from the Department of Energy Rocky Flats Field Office (DOE/RFFO) and the National Institute of Standards and Technology (NIST) at Boulder, Colorado, to develop and refine the technology needed for safe and effective processing of actinide-containing solid waste at the Rocky Flats Environmental Technology Site (RFETS).

LANL contributions were fourfold. Task 1 was to demonstrate the effectiveness of a one-sixth-scale mixer (relative to a mixer outlined in a related NIST report[1]) and to determine the optimal particle size for achieving a homogeneous mix of particles. Task 2 was to determine whether operation of the shredder/mixer at below the industry standard temperature of −40°C would be required to prevent volatile materials from escaping the five predetermined oily matrix materials. Tasks 1 and 2 followed the code of federal regulations (40 CFR 7.1.3) and solid waste regulations (SW-846) for sampling wastes. Task 3 was to demonstrate, by both modeling and experimentation, safe cryogenic grinding in a glovebox. Task 4 was to prepare a report on our findings.

Five mixed-matrix materials representing the types of contaminated waste common at RFETS were selected as test materials for the development of the processes. These materials were Kimwipes®, rubber gloves, cloth coveralls, Tyvek™ coveralls, and plastic drum liners.

Task 1—Homogeneity of particle mix. The objectives of Task 1 were threefold:

- To determine the optimal size of particles for a 10-g sample that will be used to determine the contents of a 55-gal. drum;

- To evaluate the effectiveness of different mixing and sampling schemes in producing a homogenous mixture in a representative 10-g sample; and

- To perform laboratory-scale tests with results that can be extrapolated to expected operations-scale conditions.

Samples of the five matrix materials were shredded to nonuniform pieces approximately 0.125 in., 0.25 in., and 0.375 in. in diameter and mixed in the one-sixth-scale mixer constructed along the designs of the NIST mixer. For comparison purposes, single-matrix materials, specifically, paper and beans, were subjected to the same tests as the selected mixed-matrix materials. For each test, the theoretical (statistical) result for an 80% confidence interval was compared with the experimental result. Test results for the

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[1] J. D. Siegwarth and J.A. Scott, "Cryogrinding Process Update," National Institute of Standards and Technology report (February, 1995).

0.375-in. particles were closest to the theoretical results, although test results for the 0.125-in. particles were comparable. Test results for the 0.25-in. particles were farthest from the theoretical results.The design of the paddle-wheel mixer apparently favored mixing the larger 0.375-in. particles and the smaller 0.125-in. particles. It is speculated that the clearances between the paddles and the housing must be set specifically to establish the optimum mixing for the particle sizes being mixed. The amount of material in the mixer and the paddle orientation also influence the mixing effectiveness. In our experimentation, it just happened that the conditions were such that the mixing effectiveness favored the larger and smaller sizes.

Because the paddle-wheel mixer did make a homogeneous mixture of both the single- and mixed-matrix materials, it will suffice to produce the needed homogeneous samples of waste. The sample size that a shredder will need to provide to the mixer will be dependent on the design of the mixer, as was demonstrated; but the design can favor a larger particle size, thereby reducing the amount of shredding necessary.

Task 2—Optimal temperature for operation of shredder/mixer. Because the mixed-matrix materials often contain volatile elements in the form of organic-species solvents, an optimal operating temperature for the shredder/mixer—a crucial design criterion—was required. Specifically, we needed to determine whether the shredder/mixer should be operated below the industry standard of −40°C to keep the volatile contents from escaping the mixed-matrix materials. The −40°C temperature is crucial because standard industrial equipment is operable at this temperature, but operation below this temperature requires using cryogenic components in place of bearings and similar parts.

The use of a residual gas analyzer (RGA) greatly enhanced the work on Task 2. The RGA facilitated the performance of a much larger variety of tests (including the temperature dependencies) requested by the DOE/RFFO staff as the project progressed and made possible the acquisition of a much greater amount of data than had been planned. This instrument is a mass spectrometer that can be used to observe gaseous species in the lower-mass ranges. The RGA provided data over a range of temperatures in the different oily matrices. We also measured the vapor pressures as a function of time. Gas and solid samples taken during the shredding and mixing process were analyzed by Chemical Science and Technology (CST) Division staff at Los Alamos. RGA samples taken during these tests were calibrated to parts-per-million (ppm) levels to estimate the amount of volatile organic material present. Because the concern about operating temperature is based on the volatility of the solvents in the mixed-matrix materials, we compared their vapor pressures at sea level with those at the higher altitudes of Los Alamos and Rocky Flats. This comparison was made to determine the effect of the oily matrices on the volatility of the solvent.

A comparison of vapor pressure measurements obtained by the RGA to vapor pressure measurements values in the literature indicated significant differences. Such differences were expected because the shredder/mixer is a dynamic system that disturbs the equilibrium, whereas the literature values are acquired at established equilibrium.

However, test results enabled us to establish the sensitivity of the RGA as in the range of the tens or hundreds of ppm, depending on the specific solvent species.

Experiments to determine the vapor pressures of the solvents in the various oily matrix materials indicated that the vapor pressures vary depending on the solvent species. However, vapor pressures are still significant at the low temperatures at which the experiments were conducted. For example, at $-40°C$ the RGA signal intensity for methylene chloride (CH_2Cl_2) alone is about 9×10^{-10}, whereas for the oily Kimwipes® matrix it is about 1.5×10^{-10}, but the vapor concentration is still on the order of 8,000 ppm above the oily matrix.

Our next set of tests for CH_2Cl_2 in the oily cloth matrix was to determine the vapor pressure as a function of time for room temperature and at $-50°C$. The boiling point of CH_2Cl_2 is above room temperature. After 5 min at room temperature, the vapor pressure is reduced by an order of magnitude. As a comparison, it takes approximately 30 min to obtain a similar result for $-50°C$. Since the solvent concentration can be related directly to the vapor pressure, the lowering of the vapor pressure equates to a loss in concentration in the matrix. This argument also follows from the higher vapor pressure at $-50°C$ at later times compared to the room temperature plot.

Additionally, we checked the vapor pressure of CH_2Cl_2 in the five matrices and Freon R113 for oily Kimwipes® that had been standing in unsealed plastic bags for 20–48 h. After these time periods, no mass spectra could be obtained. (For CH_2Cl_2, the sensitivity is on the order of 20 ppm; and for Freon [$CCl_2F\text{-}CClF_2$] R113, the sensitivity is about 200 ppm.)

The cryoshredder that we built to do the volatility studies was combined with the paddle-wheel mixer used in Task 1. Temperatures were measured with thermocouples placed in numerous positions, and data were collected using LabVIEW© software. A template of the LabVIEW screen displays on the computer screen temperature measurements with thermocouple placement during the experiments. Strip chart-type data output is captured during the test and then plotted. Sampling for the volatile solvent and the solvent in the solid followed a procedural process for sampling that was dictated by CST personnel. We ran two spiked samples through this procedure. ("Spiked" refers to adding a known amount of a volatile organic compound to solid materials and mixing these together. After processing, the solid materials are analyzed to determine the effects of the organic compound.) The CST analysis for these results showed that the organic compounds were present in the solid matrix after the cryoshredding, but that the quantities were less than the original spiked materials. The analysis of the gas sample taken during the processing also showed large quantities of organic compounds. This confirmed the indication from the RGA during processing, which showed a significant solvent vapor pressure. So, there is a significant loss of solvent during the process.

In conclusion, it became obvious that there were separate regimes for the operation of the complete system that need to be considered in connection with this volatility concern. The RGA results show that in a very short period of time (5 min) at room temperature a significant amount of gas will be released from the oily matrix materials. This release of

gas occurs even when the solvents have boiling points above room temperature. Therefore, even though the cryogenic shredder may be operated at −40°C, there will be a significant amount of solvent material volatilized while opening the drums and bags and while performing the warmup of the matrix material for repackaging. This suggests that one needs to freeze constituents immediately, or at least as soon as possible. In any event, one will see a significant amount of vapor pressure for a large number of species at and below −40°C. Therefore, monitoring for solvents on-line, as part of the glovebox system, may be a way of capitalizing on the volatility of the organic solvents. One may be able to "screen" materials as they are processed in order to determine whether they should be analyzed for organics by the use of an RGA system.

It should be noted that the lower-boiling species that are less than room temperature (for example, methyl chloride CH_3Cl, which boils at –24.2°C) have such high vapor pressures that it was determined that they could not be effectively loaded into a matrix for testing. The CST personnel who performed the gas and solid testing, as well as other people throughout the Laboratory, were consulted in order to come up with an appropriate method to load these high-vapor-pressure species into the predetermined matrices. No such method was found. If we are to give further consideration to these low-boiling-point species, the exact matrix needs to be identified. It is probable that some of the species are generated by radiolytic decay of plastics. Another possibility is that the solvent may be a component in the production of the plastic. There may be other possibilities as well.

Task 3—Cryogenic demonstration in a glovebox. The objective of Task 3 was to do a cryogenic grinding demonstration in a glovebox in the Los Alamos Plutonium Facility (Building PF-4, Technical Area [TA]-55). As part of this demonstration, we split the tasks into two categories, experimental and modeling. The result of this effort will enhance future designing at RFETS of a system that includes many safety considerations. Experimental work at Los Alamos included the design and implementation of a pressure feedback liquid nitrogen (LN_2) introduction system into the glovebox, controlled gas pressurization tests inside the box, LN_2 spill tests in the glovebox, and actual cryogenic grinding of in-line flow-through Hytrex^{TM} filters in the glovebox. Modeling characterized the effect of the use of cryogenic LN_2 on glovebox negativity and on thermal-induced stresses. Analysis also predicted the thermal performance of the equipment for the expected operating conditions. All of the experimental work was used to confirm model predictions. A significant number of nonradioactive environment tests also were done before the cryogrinder was installed in the glovebox.

Calculations for the glovebox LN_2 introduction system are presented in Section 3 of this report. Basically, the LN_2 introduction system is controlled by the operator using cryogenic solenoid valves. The system senses a loss of pressure negativity in the glovebox and automatically closes these valves. As part of the LN_2 control in the glovebox, we constructed a dewar and a containment pan. The pan was designed, based on the modeling, to have a surface area of 2000 cm^2. The limited surface area is discussed in the modeling part of this report.

The glovebox ventilation tests were done to determine the flow capacity of our glovebox; i.e., with our model, we could determine how much LN_2 could be spilled in the glovebox. Flow rate of gaseous nitrogen (GN_2) into the glovebox was as high as 35 standard cubic feet per minute (scfm).

LN_2 spill tests in the glovebox for our dewar size of 2 L (test volumes up to 1.5 L) resulted in negativity losses of about 0.1 in. of water in the 2000-cm^2 pan. These results are mainly used to confirm the model. For comparison, the glovebox total negativity is about 0.6 in. of water.

We did cryogenic grinding of 12 Hytrex filters. Three of these ground radioactive filters were sent for study to researchers in the field of combustibles. The other nine filters were disposed of as radioactive. The Hytrex filters come from processing and are moist. The freezing of a filter uses about 1 L of LN_2. The filter is best ground at a temperature that is between 77 K and room temperature (293 K). The cryogenic grinding apparatus that was used in the glovebox was a modified snow cone machine. As with Task 2, we used LabVIEW$^©$ software and continuously obtained temperature and pressure readings for inside the glovebox. Some of this data is presented and interpreted in this report.

In conclusion, the glovebox tests confirmed the model calculations, and we demonstrated successfully and safely the use of such a system in a glovebox. Much of our data, experience, and the modeling will help the design and implementation of the RFETS cryogenic grinding system. Another result of our work is the discovery that the operating temperature for the cryogrinder was best between 77 K and 273 K. Therefore, one may base the operating temperature of the grinder on these results instead of basing it on volatility. When grinding the filters, we also observed a pressure gain caused by a significant release of GN_2 into the box. After grinding, the filter temperature was typically less than $-50°C$.

Other considerations that we were asked to investigate were the effect of the process on volume reduction and the use of the process as sample feed for alternatives to incineration. Some items, such as 2-L bottles, will show volume reduction; but the size of the particle produced will dictate the amount of reduction (i.e., a 0.375-in. particle is better for volume reduction than a 0.125-in. particle). In general, many matrices actually increase in volume for the various particle sizes. Alternatively, the particles generated from this process are much better, perhaps ideal, for combustible processes. A 0.125-in. size is probably better than a 0.375-in. size for these processes. Finally, it should be noted that this process can be modified for various purposes. For example, the process could provide small particles for hydrothermal or oxidation reduction processes.

In general, we accomplished our tasks. We demonstrated homogeneity; we studied the volatility of the volatile organic compounds (VOCs) at different temperatures for different matrices; and we performed a safe cryogenic operation in a radioactively contaminated glovebox. Moreover, we collected considerably more data/results than we initially expected.

APPLICATION OF CRYOGENIC GRINDING TO ACHIEVE HOMOGENIZATION OF TRANSURANIC MIXED WASTES

by

William H. Atkins, Dallas D. Hill, Mary E. Lucero,
Lorenzo Jaramillo, Horacio E. Martinez,
James T. McFarlan, Arthur N. Morgan,
Timothy O. Nelson, F. Coyne Prenger,
Wilfred R. Romero, and Len H. Stapf

ABSTRACT

This paper describes work done at Los Alamos National Laboratory (LANL) in collaboration with the Department of Energy Rocky Flats Field Office (DOE/RFFO) and with the National Institute of Standards and Technology (NIST), Boulder, Colorado. Researchers on this project have developed a method for cryogenic grinding of mixed wastes to homogenize and, thereby, to acquire a representative sample of the materials. There are approximately 220,000 waste drums owned by the Rocky Flats Environmental Technology Site (RFETS)—50,000 at RFETS and 170,000 at the Idaho National Engineering Laboratory. The cost of sampling the heterogeneous distribution of waste in each drum is prohibitive. In an attempt to produce a homogeneous mixture of waste that would reduce greatly the cost of sampling, researchers at NIST and RFETS are developing a cryogenic grinder. The Los Alamos work herein described addresses the implementation issues of the task. The first issue was to ascertain whether samples of the "small particle" mixtures of materials present in the waste drums at RFETS were representative of actual drum contents. Second, it was necessary to determine at what temperature the grinding operation must be performed in order to minimize or to eliminate the release of volatile organic compounds present in the waste. Last, it was essential to evaluate any effect the liquid cryogen might have on the structural integrity and ventilation capacity of the glovebox system. Results of this study showed that representative samples could be and had been obtained, that some release of organics occurred below freezing because of sublimation, and that operation of the cryogenic grinding equipment inside the glovebox was feasible.

1. PARTICLE SAMPLE SIZE

1.1. Objective

The objectives of Task 1: Particle Sample Size were as follows:

- To determine how the size of particles in a 10-g sample affects its usefulness in representing the contents of a 55-gal. drum;

- To evaluate the effectiveness of different mixing and sampling schemes in producing a homogeneous mixture and a representative 10-g sample; and

- To conduct laboratory-scale tests whose results could be extrapolated to operations-scale conditions.

We constructed a one-sixth-scale version of the National Institute of Standards and Technology (NIST) conceptual designed mixer and used it to mix various materials of the type and size expected to be encountered in actual use at Rocky Flats Environmental Technology Site (RFETS). By varying the mixing and sampling configurations, we gained insight into the optimal construction and operating parameters for a full-scale mixer.

After establishing a protocol for conducting the sampling and mixing processes, we conducted tests to quantify the accuracy and precision with which a sampling scheme could produce a representative sample. Although the total concentrate leachate procedure (TCLP) requires a sample of at least 100 g and may require two or three samples, we used a 10-g sample diluted in a 100-mL solution. Federal regulations (40 CFR 7.1.3) require particles smaller than 1 cm in their smallest dimension, and commercial shredders are unlikely to produce particles smaller than 0.0625-in. in diameter. A 10-g sample would probably contain no more than 450 particles of the required size[1]. We conducted warm testing only for the first task and did not cryogenically cool the samples. Later sections of this report detail cryogenic grinding experiments and their results.

1.2. Equipment Design and Materials Selection

To obtain equipment to do the particle generation, mixing, and analysis, we first attempted to procure from a commercial vendor a shredder or granulator that could produce samples from the soft materials needed for the experiments. Contacts with a number of companies indicated that their equipment was high in cost ($15,000 to $22,000 for a small shredding unit) and limited in availability (delivery times ranged from eight weeks to many months). For these reasons, we asked Nelmor Company (whose cost and time estimates met our schedule and budget needs) to shred the materials we would supply. To evaluate the mixing characteristics of a paddle-wheel mixer being designed for the project, we used two office paper shredders to produce 0.0625-in. and 0.125-in. particles of paper, cloth, and Tyvek™ samples for the first mixer tests.

Using the design by Siegwarth[1], we constructed a laboratory-scale mixer from a cylindrical air compressor tank approximately 1 ft in diameter and 20 in. in length (see Fig. 1-1). We mounted four pairs of paddles along a shaft attached on the axis of the tank and installed a variable-speed motor to drive the shaft at various speeds. The paddles (4-in. by 4-in. square) were rotated to an angle of plus and minus 20 to 25 degrees with respect to their direction of motion. This rotation ensured that the sample materials would be pushed toward the center of the mixer as they were lifted and tossed.
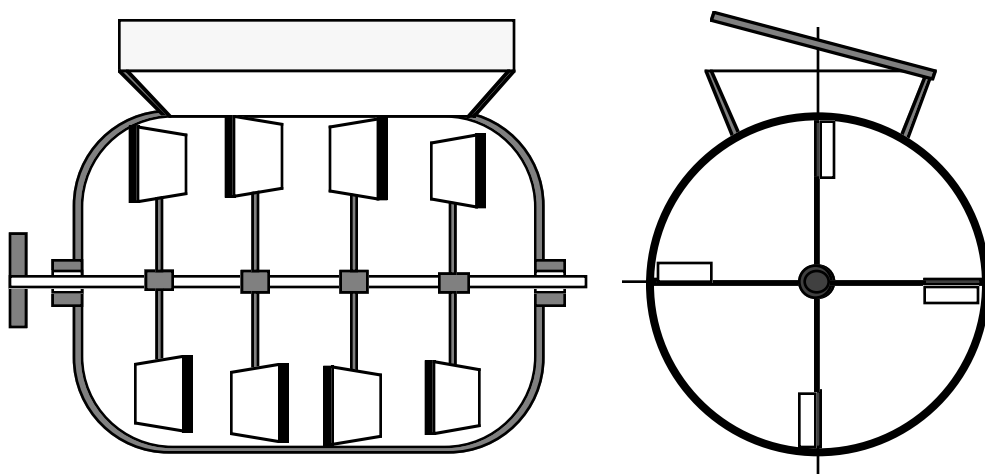
Fig. 1-1. Schematic of laboratory-scale mixer for testing particles of various sizes.

Materials selected for testing were those that most commonly require disposal by the method under consideration. They were plastic drum liners, cloth coveralls, Kimwipes®, latex gloves (rubber), and Tyvek coveralls contaminated with a variety of solvents.

1.3. Analysis Methods

After each mixer run, we took several samples. We characterized each sample by determining the specified percentage of each of the materials in the sample. We evaluated the accuracy of sample measurements by comparing the mean measurement to the known value. If, as hoped, the sample estimates fell in a normal distribution, the sample mean would equal the population mean. Table 1-1 defines the relevant statistical symbols used in this analysis.

The precision with which sample measurements represent the known value is characterized by the confidence interval, which is represented by the error bars associated with the sample mean. Given a desired confidence of 80%, we calculated the interval around the sample mean that, 80% of the time, will contain the population mean. Chapter 9 of the relevant solid waste

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[1] J. D. Siegwarth and J.A. Scott, "Cryogrinding Process Update," National Institute of Standards and Technology report (February, 1995).

regulation SW-846[2] calls for an 80% confidence interval for the purposes of evaluating solid wastes against regulatory thresholds.

As an example, the 80% confidence interval for plastic in a mixture with an average weight of 21.75% of total, using 6 samples, and with a sampling deviation of 1.118% is

$$\overline{x} \pm t_{n-1;\alpha/2} * s_{\overline{x}} = 21.75 \pm t_{5;.1} * \frac{1.12}{\sqrt{5}} = 21.75 \pm 1.476 * .5$$

(The variable t must be looked up in a t-distribution table.) Thus, there is 80% confidence that the percentage of plastic in the mixture is between 21.01% and 22.49%.

Table 1-1. Statistical Symbols and Terms

Symbol	Definition
x	Variable, such as the percentage of plastic in drum
x_i	Individual measurement of x (one sample)
μ	Population mean (true value of x)
n	Number of samples
$\overline{x}$	Mean of sample measurements
$s^2 = \dfrac{\sum_{i=1}^{n}(x_i - \overline{x})^2}{n-1}$	Variance of sample
$s = \sqrt{s^2}$	Standard deviation of sample
$s_{\overline{x}} = \dfrac{s}{\sqrt{n}}$	Standard deviation of mean of sample
$\overline{x} \pm t_{n-1;\alpha/2} s_{\overline{x}}$	Confidence interval for m, where t is from the t-distribution list

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[2] "Sampling Plan," in *Test Methods for the Evaluation of Solid Waste, Physical/Chemical Methods*, 3rd edition, EPA Publication SW-846, 955-001-00000-1 (Washington, D.C.: Government Printing Office).

1.4. Sampling Methods

Samples consisting of particles in each of the three sizes produced by initial shredding were mixed. Approximately equal parts by weight of each type of material were randomly introduced into the mixer; thus the total sample in a given run was approximately 20% plastic drum liner particles, 20% cloth coverall particles, 20% Kimwipes particles, 20% latex glove particles, and 20% Tyvek coverall particles. The total amount of material in the mixer was typically just less than half the volume of the mixer. Visual inspection indicated that this amount of material provided the best agitation and mixing, for samples consisting of the larger-sized particles. However, adequate mixing of the 0.125-in. particles required larger quantities of the materials.

For each test, the mixer was run for 10 min at approximately 90 rpm. At the end of each mixing period, six 10-g samples were taken from the center of the mixer for each test. Figure 1-2 shows the mixer after mixing the 0.125-in. material.

The samples proved difficult for separating into the constituent materials. The materials were too fine to separate by hand, and the cloth particles were typically a fine lint that adhered to all other materials. After experimenting with different methods, we found that, because of differences in density (see Fig. 1-3), simply stirring the sample in a beaker of water caused the cloth and Kimwipes particles to sink to the bottom, while the Tyvek, latex, and plastic particles floated at the top. After removing the particles from the water and allowing them to dry, we could remove the latex by hand. Thus, we could separate the 0.25-in. and 0.375-in. samples into three components: cloth/paper, Tyvek/plastic, and latex. We were unable to separate the latex particles from the 0.125-in. samples, so these samples were separated into only two components: cloth/paper and Tyvek/plastic/rubber.
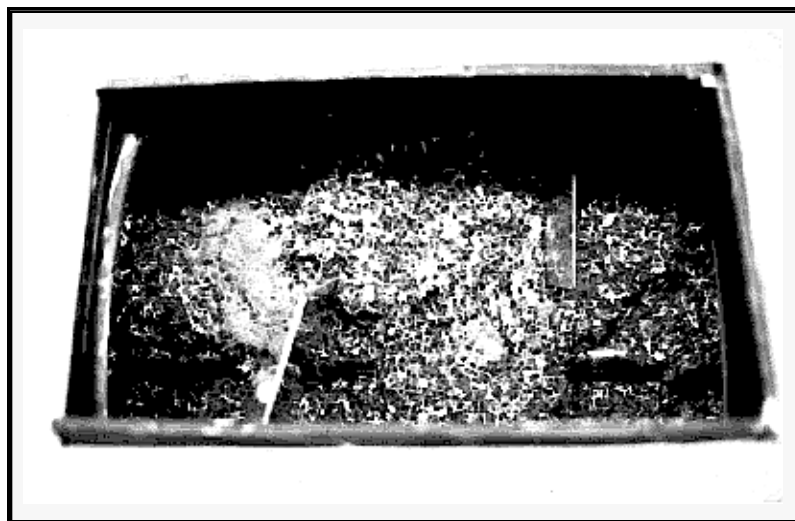
Fig. 1-2. Mixer and 0.125-in. material.

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Fig. 1-3. Separation of materials in beaker of water.

1.5. Materials Test Results

The degree to which a sample represents the entire mixer contents can be determined by establishing its accuracy and precision. The accuracy of the sample is related to the difference between the sample characteristics acquired after mixing and the sample characteristics known before mixing. Precision is indicated by the standard deviation and confidence interval of assigned values of the pre- and post-mixing samples. Because the paper samples and the 0.125-in. samples had only two components after mixing, we performed calculations for one of the components and took the other to be symmetrical.

We chose the 80% confidence interval because it is specified by regulation (SW-846) for the purpose of evaluating solid wastes for chemical contamination, and we performed the calculation as required by the regulation. If the value is 2.08, as it is for the latex component of the 0.375-in. sample, there is an 80% probability that the true percentage of latex in the mixer is the sample mean (23.07%) plus or minus 2.08.

1.5.1. Paper Tests

Before receiving shredded materials from Nelmor, we used shredded paper particles, approximately 0.125 in. by 0.25 in., as mixing samples. After mixing known quantities of white and blue paper, we extracted 10-g samples from the mixer's center and manually separated them into white and blue constituents. We conducted several mixing tests with paper samples in order to set gross mixing parameters. By visually observing the mixing in progress, we were able to

vary mixer speed, paddle orientation, mixing time, and total amount of material in the mixer. After setting these mixer parameters, we conducted additional tests, extracted mixed samples, and manually separated the constituents. Results of paper mixing, shown in Tables 1-2 and 1-3, indicate good accuracy and precision—less than 2% variation from the true value. Mixing the paper for 5 min gave the best absolute accuracy.

Table 1-2. Results of Paper Mixing Test 1

Mixer Contents		
	(g)	(%)
White	807.3	85.60
Blue	135.8	14.40
Total	943.1	100.00

	Weight of Sample		Percentage of Sample	
Sample	White	Blue	White	Blue
1	8.696	1.346	86.60	13.40
2	8.737	1.268	87.33	12.67
3	8.617	1.325	86.67	13.33

$t(n = 3, 80\%$ confidence) -1.886

Precision		White
	Mean	86.87
	Standard Deviation	0.40
	80% Confidence Interval (±)	0.44

Accuracy		
	True %	85.60
	Sample %	86.87
	Difference	−1.26

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Table 1-3. Results of Paper Mixing Test 2*

Mixer Contents		
	(g)	(%)
White	882.5	87.94
Blue	121.0	12.06
Total	1003.5	100.00

	Weight of Sample		Percentage of Sample	
Sample	White	Blue	White	Blue
1	9.088	1.373	86.88	13.12
2	8.956	1.408	86.41	13.59
3	9.002	1.109	89.03	10.97

t(n=3, 80% confidence)-1.886

Precision		White
	Mean	87.44
	Standard Deviation	1.40
	80% Confidence Interval ($\pm$)	1.52

Accuracy		
	True %	87.94
	Sample %	87.44
	Difference	0.50

*Shredded pieces of white and blue paper were mixed for 1 min at 90 rpm, after which mixing three samples were taken. The different-colored pieces were separated manually.

1.5.2. Bean Tests

Samples consisting of beans and peas offered a higher-density alternative to paper samples. Such samples are also easy to count. Because beans and peas weigh more than paper by volume, we did not fill the mixer to the same level we had used with paper. When sampling revealed that a 10-g sample would amount to only about 70 beans and peas, we conducted the test with 100-g samples. Results of bean and pea mixing, shown in Tables 1-4 and 1-5, indicate a definite lower limit on the number of particles needed to make up the sample. Table 1-4 shows the results for 10-g samples, and Table 1-5 shows the results for 100-g samples.

1.5.3. Nelmor Materials Tests

The Nelmor Company shredded the Tyvek coveralls, cloth coveralls, Kimwipes, latex gloves, and plastic drum liners we provided and, for each material type, returned 500 g–1000 g of particles in each of three sizes: 0.125-in., 0.25-in., and 0.375-in. The size was established as the particle passing through a square mesh of that size. We had dyed the Kimwipes material red or black so that we could readily distinguish it from the white Tyvek material.

Table 1-4. Results of Bean Mixing Test 1*

Mixer Contents	(g)	(%)
Black Turtle Beans	4865.7	68.10
White Navy Beans	1353.2	18.94
Green Split Peas	926.2	12.96
Total	1080.0	100.00

	Weight of Sample			Percentage of Sample		
Sample	Black	White	Green	Black	White	Green
1	8.253	0.616	1.508	79.53	5.94	14.53
2	8.035	1.716	1.464	71.65	15.30	13.05
3	7.172	2.387	0.58	70.74	23.54	5.72

t(n=3, 80% confidence)-1.886

Precision

	White
Mean	14.93
Standard Deviation	8.81
80% Confidence Interval (±)	9.59

Accuracy

	White
True %	18.94
Sample %	14.93
Difference	4.01

*Three types of small beans and peas were mixed for 5 min at 90 rpm, after which 10-g samples were taken. Only white beans were counted from the sample.

Table 1-5. Results of Bean Mixing Test 2*

Mixer Contents	(g)	(%)
Black Turtle Beans	4865.7	68.10
White Navy Beans	1353.2	18.94
Green Split Peas	926.2	12.96
Total	7145.1	100.00

	Weight of Sample			Percentage of Sample		
Sample	Black	White	Green	Black	White	Green
1	66.946	22.078	10.185	67.48	22.25	10.27
2	67.44	17.872	8.963	71.54	18.96	9.51
3	60.738	19.64	7.79	68.89	22.28	8.84

t(n = 3, 80% confidence) –1.886

Precision

	White
Mean	21.16
Standard Deviation	1.91
80% Confidence Interval (±)	2.08

Accuracy

	White
True %	18.94
Sample %	21.16
Difference	–2.22

*Same as Bean Mixing Test 1, but with three additional 100-g samples taken.

The results of mixing and sampling the materials shredded by Nelmor were less accurate than the results of mixing and sampling paper or beans. The materials shredded by Nelmor occasionally formed clumps and were separated less easily into components. For example, latex particles in one of the bags received from Nelmor were clumped, apparently as a result of the heating that occurred during shredding. We treated clumped particles by freezing them with liquid nitrogen (LN_2) and grinding them by hand. We separated the frozen and ground components by stirring them in water, as described previously; but a small amount of cross-contamination of all components between matrices remained in these samples.

Tables 1-6, 1-7, and 1-8 show the mixing results for the materials shredded by Nelmor for the 0.125-in., 0.25-in., and 0.375-in. particles, respectively. Reasonable values were obtained for all tests. However, the accuracy for the 0.25-in. particles was poorer than the accuracy for both the 0.125-in. particles and the 0.375-in. particles. Such a finding indicates that we cannot assume a universal trend toward better mixing as particle size decreases. Instead, optimal results are likely to be obtained by tailoring the mixing parameters.

Table 1-6. Results of Mixing Test for 0.125-in. Particles[*]

Mixer Contents		
	(g)	(%)
Cloth	580.5	30.62
Kimwipes	407.0	21.47
Tyvek	292.7	15.44
Plastic	280.1	14.78
Rubber	335.4	17.69
Total	1895.7	100.00

	Weight of Sample		Percentage of Sample	
Sample	Cloth/ Kimwipes	Tyvek/plastic/ latex	Cloth/ Kimwipes	Tyvek/plastic/ latex
1	5.066	5.377	48.51	51.49
2	5.021	5.464	47.89	52.11
3	4.759	5.220	47.69	52.31
4	5.242	5.477	48.90	51.10
5	4.510	4.581	49.61	50.39
6	5.607	6.121	47.81	52.19

t(n = 6, 80% confidence) –1.476

		Cloth/Kimwipes	Tyvek/plastic/rubber
Precision	Mean	48.40	51.60
	Standard Deviation	0.75	0.75
	80% Confidence Interval (±)	0.45	0.45
Accuracy	True %	52.09	47.91
	Sample %	48.40	51.60
	Difference	3.69	–3.69

[*]The ingredients were mixed for 10 min at 90 rpm, after which mixing six samples were taken. Each sample was separated into two components: cloth/Kimwipes and Tyvek/plastic/rubber.

Table 1-7.   Results of Mixing Test for 0.25-in. Particles*

Mixer Contents		
	(g)	(%)
Cloth	201.0	20.40
Kimwipes	164.2	16.66
Tyvek	219.4	22.27
Plastic	194.7	19.76
Latex	206.0	20.91
Total	985.3	100.00

	Weight of Sample			Percentage of Sample		
Sample	Cloth/ Kimwipes	Tyvek/ plastic	Rubber	Cloth/ Kimwipes	Tyvek/ plastic	Latex
1	3.827	4.647	1.392	38.79	47.10	14.11
2	2.376	4.452	2.417	25.70	48.16	26.14
3	2.503	4.834	1.333	28.87	55.76	15.37
4	3.539	4.465	1.219	38.37	48.41	13.22
5	2.365	3.965	3.384	24.35	40.82	34.84
6	2.464	4.325	1.890	28.39	49.83	21.78

t(n = 6, 80% confidence) –1.476

Precision		Cloth/ Kimwipes	Tyvek/ plastic	Latex
	Mean	30.74	48.35	20.91
	Standard Deviation	6.30	4.80	8.46
	80% Confidence Interval (±)	3.80	2.89	5.10

Accuracy		Cloth/ Kimwipes	Tyvek/ plastic	Latex
	True %	37.06	42.03	20.91
	Sample %	30.74	48.35	20.91
	Difference	6.32	–6.32	0.00

*The ingredients were mixed for 10 min at 90 rpm, after which mixing six samples were taken. Each sample was separated into three components: cloth/Kimwipes, Tyvek/plastic, and latex.

Table 1-8. Results of Mixing Test for 0.375-in. Particles*

Mixer Contents		
	(g)	(%)
Cloth	212.7	19.69
Kimwipes	213.8	19.80
Tyvek	216.0	20.00
Plastic	210.7	19.51
Latex	226.8	21.00
Total	1080.0	100.00

Sample	Weight of Sample			Percentage of Sample		
	Cloth/ Kimwipes	Tyvek/ plastic	Latex	Cloth/ Kimwipes	Tyvek/ plastic	Latex
1	3.606	4.117	2.276	36.06	41.17	22.76
2	3.796	3.839	1.839	40.07	40.52	19.41
3	3.997	4.963	2.096	36.15	44.89	18.96
4	3.424	3.873	2.201	36.05	40.78	23.17
5	3.386	3.792	2.638	34.49	38.63	26.87
6	3.443	3.989	2.786	33.70	39.04	27.27

$t(n = 6, 80\% \text{ confidence}) -1.476$

Precision

	Cloth/ Kimwipes	Tyvek/ plastic	Latex
Mean	36.09	40.84	23.07
Standard Deviation	2.20	2.22	3.53
80% Confidence Interval (±)	1.32	1.34	2.13

Accuracy

	Cloth/ Kimwipes	Tyvek/ plastic	Latex
True %	39.49	39.51	21.00
Sample %	36.09	40.84	23.07
Difference	3.40	−1.33	−2.07

*The ingredients were mixed for 10 min at 90 rpm, after which mixing six samples were taken. Each sample was separated into three components: cloth/Kimwipes, Tyvek/plastic, and latex.

Findings further indicate that the precision of the sample measurements was better than their accuracy. Good precision, of course, indicates consistency. However, accuracy is more desirable than precision because consistently inaccurate measurements may still be precise. Extracting samples from random locations probably would increase the accuracy of the findings. For these tests, we routinely extracted samples from the center of the mixer because material at other locations was visibly less well mixed. This biased sampling apparently resulted in reduced accuracy. Figures 1-4 through 1-6 show that precision increases with the number of samples, a finding that should be universally true. The greatest gain in precision occurs when three samples are used.
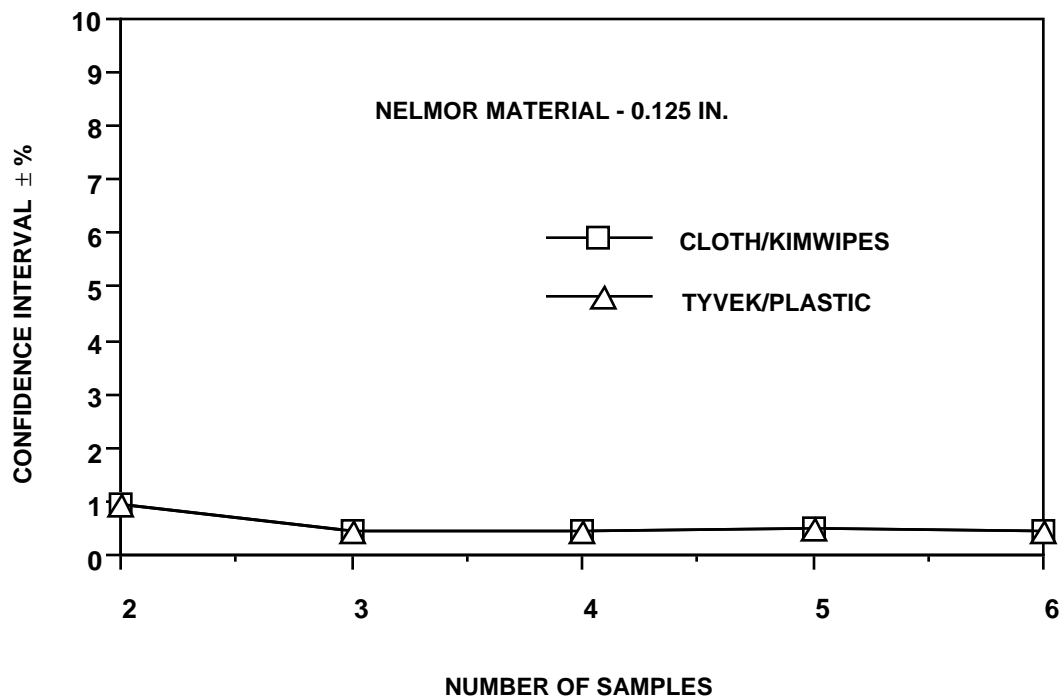
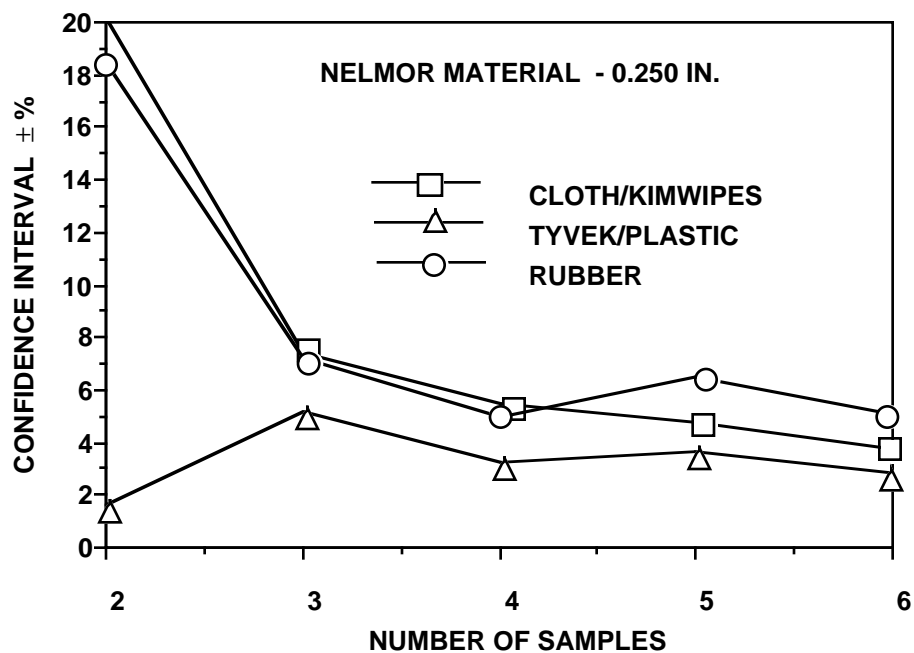Fig. 1-4. Confidence interval for 0.125-in. particles.

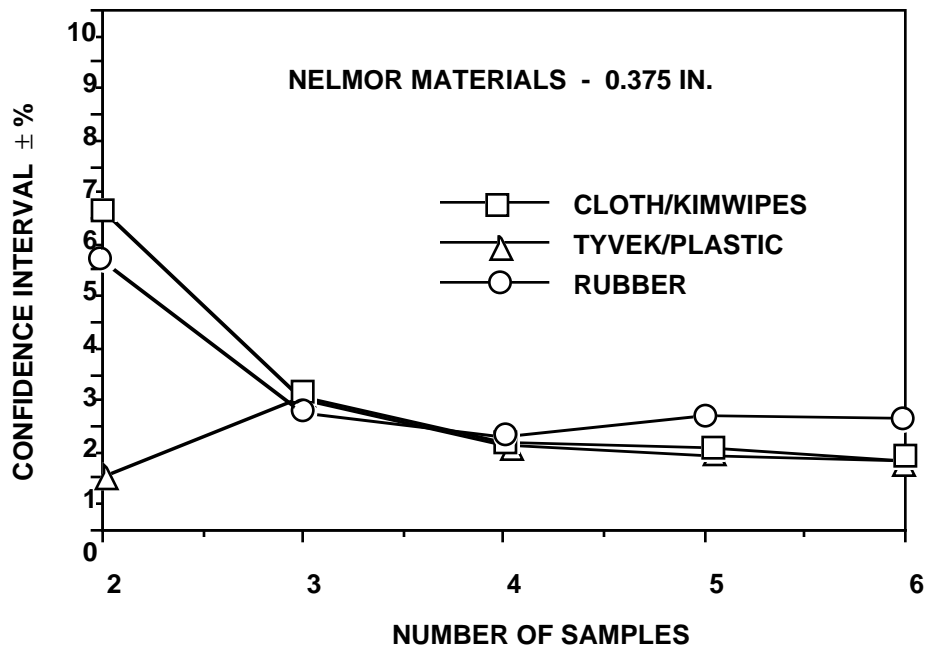Fig. 1-5. Confidence interval for 0.25-in. particles.

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Fig. 1-6. Confidence interval for 0.375-in. particles.

1.6. Conclusions

Equipment characteristics (such as paddle design, speed, and volume) and duration of the mixing were more significant contributors than particle size to sample accuracy. A paddle-type mixer seems to be adequate, but the paddle orientation along the axis of rotation and the orientation of the mounting spokes should be variable. Also, the paddles should be variable in speed. Tests similar to those reported here should be performed to determine the optimal settings for variables. The mixer volume should be twice the size of the expected contents and should be filled to the level that produces the desired homogeneous mix.

All the particle sizes tested appeared suitable for producing a 10-g sample representative of a larger mixture. Special attention should be given to mixers in which particles accumulating in certain positions receive insufficient mixing. In the mixer design used for this study, poorly mixed accumulations were observed close to the end caps and at the opposite end from the end caps. Insufficient quantities of particles and particles too small to be picked up by the paddle because of the clearance between the mixer wall and paddle also caused poorly mixed particles. In addition to the overall ease of running cryogen-embrittled materials through the shredder, cryogenic techniques also may improve the mixing operation by ensuring that the particles remain discrete. Samples extracted either randomly or systematically from distributed positions in the mixer will provide better accuracy, even if such samples are analyzed as a single sample.